(54) Title: HIGHLY PURIFIED LIQUID PERFLUORO-N-ALKANES AND METHOD FOR PREPARING

(57) Abstract: The present invention is drawn to liquid perfluoro-n-alkanes that are highly transparent to UV wavelengths ranging from about 150 nm to 165 nm, and to the method by which high transparency may be obtained. The liquid perfluoro-n-alkanes of the invention are useful in optical couplants, optical cements, optical elements, optical inspection media for semiconductor wafers and devices, and immersion photolithography at 157 nm exposure wavelength

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TITLE

HIGHLY PURIFIED LIQUID PERFLUORO-n-ALKANES AND METHOD FOR PREPARING

FIELD OF THE INVENTION

5   The present invention is drawn to liquid perfluoro-n-alkanes that are highly transparent to UV wavelengths ranging from about 150 nm to 165 nm, and to the method by which high transparency may be obtained. The liquid perfluoro-n-alkanes of the invention are useful in optical couplants, optical cements, optical elements, optical inspection media for

10   semiconductor wafers and devices, and immersion photolithography at 157 nm exposure wavelength.

BACKGROUND

Much progress in the electronics industry comes from circuit size reduction. This is most directly accomplished by running photolithographic

15   processes at ever-shorter wavelengths of light. The electronics industry is currently implementing photolithographic processes employing wavelengths in the so-called "vacuum ultra-violet" (VUV). Processes using 193 nanometer (nm) light are undergoing commercialization while 157 nm wavelength light is under development as a next generation candidate.

20   One new development in the field is so-called immersion photolithography at 157 nm exposure wavelength as described in Switkes et al, *J. Vac. Sci. Technol. B*, 19 (6), 2353 6, Nov./Dec. 2001; and, M. Switkes et al, "Resolution enhancement of 157-nm photolithography at 157 nm exposure wavelength by liquid immersion", *Proc. SPIE* Vol. 4691,

25   pp. 459-465 (2002). In immersion photolithography at 157 nm exposure wavelength, the optical source, the target surface, or the entire lithographic apparatus is immersed in a highly transparent high refractive index liquid. Realization of the potential benefits of this technology is dependent upon identifying liquids with exceptionally high transparency in the VUV with

30   excellent photochemical stability, as described, for example, in M. Switkes, R. R. Kunz, M. Rothschild, R. F. Sinta, P. M. Gallagher-Wetmore, and V. J. Krukonis, "Liquids for immersion photolithography at 157 nm exposure wavelength at short wavelengths", *Proc. SPIE* Vol. 5040, 690-699 (2003).

Switkes et al, *Microlithography World*, May 2003, pp. 4ff, disclose that 157 nm light in a high refractive index medium can simulate the effects of much shorter wavelength light for photolithographic purposes.

5   Considerable emphasis has been placed on identifying organic polymeric compositions suitable for use in the VUV. WO 0185811 and WO 137044 disclose fluorinated polymeric compositions having high transparency at 157 nm. Considerably less emphasis has been placed upon lower molecular weight organic liquids, which may be employed as an immersion medium in immersion photolithography in which a liquid

10   medium is used between the projection lens of the optical stepper and the photoresist-coated substrate (typically a silicon wafer), which will receive and detect the photolithographic image. Whether polymeric or not, any material residing in the light path between the source and the target needs to be highly transparent and photochemically stable at VUV wavelengths.

15   As disclosed in the references hereinabove cited, suitable liquids can also be used as inspection media for immersion inspection of patterned objects such as semiconductor wafers, wherein the effectively reduced wavelength will produce higher resolution imaging of small size defects.

According to Switkes et al, "Liquids for immersion photolithography

20   at 157 nm exposure wavelength at short wavelengths," *op.cit.*, it is desirable that an immersion liquid layer be at least 1mm thick for mechanical reasons and at least 95% transparent for good optical performance. A reasonable estimate of the needed absorbance for an immersion liquid is A/cm = 0.22, as determined from the equation

25     $$A/cm \leq [\log_{10}(To/T)]/h = [\log_{10}(100\%/95\%)]/0.1 = 0.22$$

Where   To = light intensity in the absence of immersion fluid

T   = light intensity with immersion fluid present

h   = distance from lens to resist in centimeters

In general, of course, the more transparent the better.

30   All known organic materials absorb to some extent at 157 nm. The issue is whether liquids can be found that are sufficiently transparent to be practical. It is known in the art that short chain hydrocarbons $H(CH_2)_nH$ and short chain fluorocarbons $F(CF_2)_nF$ are relatively transparent

compared to their longer-chain homologues. See for example, B. A.
Lombos et al, Chemical Physics Letters, 1, 42 (1967); G. Belanger et al,
Chemical Physics Letters, 3(8), 649(1969); and K. Seki et al, *Phys.
Scripta*, 41, 167(1990).

5   E. Albrecht et al, CERN Document Server: Preprints (2002) 1-14,
ep/ep-2002-099, 16 Dec 2002,
(URL:http://documents.cern.ch/archive/electronic/cern/preprints/ep/ep-
2002-099.pdf.) discloses that gas phase perfluoro-n-alkanes up to
perfluorobutane are sufficiently transparent below 160 nm for use as
10   Cherenkov detectors particularly when impurities such as oxygen, water,
and hydrocarbons have been removed. However, gases exhibit very low
refractive index and therefore are not suitable for use in immersion
photolithography at 157 nm exposure wavelength.

          Perfluoroalkane liquids are known. Perfluoro-n-pentane and
15   perfluoro-n-hexane are available commercially at purities in excess of
99%.

          Liquids having the high transparency of perfluoro-n-alkane vapors
but with higher refractive index, and the desirable photochemical stability
for practical use in immersion photolithography at 157 nm exposure
20   wavelength, and other applications in the VUV are desired.

SUMMARY OF THE INVENTION

          The present invention provides a composition consisting essentially
of a perfluoro-n-alkane liquid characterized by a water concentration of
less than 10 ppm, an oxygen concentration of less than 10 ppm, and an
25   absorbance at 157 nanometers in the range of 0.1-10 cm^{-1}, said perfluoro-
n-alkane liquid selected from perfluoro-n-pentane, perfluoro-n-hexane, and
mixtures thereof.

          The present invention further provides processes for preparing a
perfluoro-n-alkane liquid having a water concentration of less than 10 ppm,
30   an oxygen concentration of less than 10 ppm, and an absorbance at 157
nanometers in the range of 0.1-10 cm^{-1}, the process comprising fractional
distillation of an as-received perfluoro-n-alkane liquid of at least 99% purity
in a grease-free distillation system, contacting a heart cut condensate

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obtained therefrom with an absorbent, and maintaining the thus contacted

condensate in an oxygen-minimized atmosphere, said perflurooalkane

liquid being selected from perfluoro-n-pentane, perfluoro-n-hexane, and

mixtures thereof; said absorbents being selected from silica gel, zeolite

5   molecular sieves, and mixtures thereof; said absorbents prior to contacting

said condensate having been subject to heating in an oxidizing

atmosphere to a temperature sufficient to drive off moisture and organic

contamination, followed by cooling and sealing in an inert, oxygen-

minimized atmosphere.

10   BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic drawing of the Harrick DLC liquid specimen

cell, showing the annular spacers, windows and related parts.

Figure 2 shows the absorbance in units of inverse centimeters for

Hexafluoropropylene Cyclic Dimer (example C1) versus wavelength

15   lambda (λ) in units of nanometers. Results below ~160 nm (dashed line)

and ~150 (solid line) exhibit saturation of the absorbance measurement.

Figure 3 shows the absorbance in units of inverse centimeters for

Perfluoro-2-methylpentane (example C2) versus wavelength lambda (λ) in

units of nanometers. Results below ~150 nm exhibit saturation of the

20   absorbance measurement.

Figure 4 shows the absorbance in units of inverse centimeters for

Perfluorooctane (example C3) versus wavelength lambda (λ) in units of

nanometers. Results below ~160 nm exhibit saturation of the absorbance

measurement.

25   Figure 5 shows the absorbance in units of inverse centimeters for

Perfluorononane (example C4) versus wavelength lambda (λ) in units of

nanometers. Results below ~180 nm exhibit saturation of the absorbance

measurement.

Figure 6 shows the absorbance in units of inverse centimeters for

30   Perfluoro(1,3-dimethylcyclohexane) (example C5) versus wavelength

lambda (λ) in units of nanometers.

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Figure 7 shows the absorbance in units of inverse centimeters for Perfluoro-trans-decalin (example C6) versus wavelength lambda (λ) in units of nanometers. Results below ~165 nm exhibit saturation of the absorbance measurement.

5   Figure 8 shows the absorbance in units of inverse centimeters for Perfluoro-n-hexane (example 1) versus wavelength lambda (λ) in units of nanometers for a sample a) loaded in Air, b) loaded in N_2, c) loaded in N_2 and shaken with water, and d) loaded in N_2, shaken with water and dried with 3A molecular sieves.

10   Figure 9 shows the absorbance in units of inverse centimeters for Perfluoro-n-pentane (example 2) versus wavelength lambda (λ) in units of nanometers for a sample a) loaded in Air (dash dot line), b) loaded in N2 (dotted line) , c) loaded in N2 and shaken with water (dashed line), and d) loaded in N2, shaken with water and dried with 3A molecular sieves (solid

15   line).

Figure 10 shows the absorbance in units of inverse centimeters for Perfluoro-n-hexane (example 3) versus wavelength lambda (λ) in units of nanometers. Results below ~150 nm exhibit saturation of the absorbance measurement.

20   Figure 11 shows the absorbance in units of inverse centimeters for Perfluoro-n-hexane (example 4) versus wavelength lambda (λ) in units of nanometers. Results below ~149 nm exhibit saturation of the absorbance measurement.

Figure 12 shows (example 4) the index of refraction in absolute

25   units for Perfluoro-n-hexane (example 4) versus wavelength lambda (λ) in units of nanometers.

Figure 13 shows the equipment for immersion contact photolithography at 157 nm exposure wavelength (example 4). (1) is the Scientech: Vector D200 laser power meter, (2) is the N_2 Purged Dry Box,

30   (3) is the Thermox Oxygen Analyzer for the Dry Box, (4) is the 157 nm Dielectric Mirror, (5) Photoresist coated silicon wafer, with photomask contacting its top surface, in petri dish, (6) Newport Air Table, (7)

translation stage for sequential exposures, (8) Gloved Access Ports, (9) Lambda Physik Optex 157 nm Excimer Laser. (example 4)

Figure 14 shows the optical apparatus for immersion contact photolithography at 157 nm exposure wavelength (example 4). (1) 157 nm

5   Dielectric Mirror , (2) Photoresist coated silicon wafer in petri dish with photomask contacting its top surface, (3) N_2 Purged Dry Box , (4) Scientech PHF25 Power Meter Head , (5) CaF_2 Beam Splitter , (6) 157nm Laser Beam at ~ 1mJ/cm^2 .

Figure 15 shows the wafer exposure stage for immersion contact

10   photolithography at 157 nm exposure wavelength (example 4). A shows the setup for contact immersion photolithography at 157 nm exposure wavelength with an immersion fluid, while B show the setup for dry contact photolithography at 157 nm exposure wavelength without the use of an immersion fluid. (1) Pyrex cover plate , (2) CaF2 Window , (3) Glass Petri

15   Dish, (4) Dry Nitrogen Environment, (5) silicon wafer substrate, (6) photoresist coating, (7) photomasks contacting the photoresist coating, (8) Immersion Fluid filled to 1mm above the wafer; the fluid thickness is not represented to scale.

Figure 16 shows (example 4) an optical micrograph of the

20   immersion contact photolithography at 157 nm exposure wavelength image of the 50 mesh grid photomask printed using Perfluoro-n-hexane as the immersion fluid with a 1mm fluid depth.

Figure 17 shows (example 4) an optical micrograph of the dry contact photolithography at 157 nm exposure wavelength image, in which

25   no immersion fluid is used, of the 50 mesh grid photomask printed.

Figure 18 shows · the absorbance in units of inverse centimeters for Perfluorooctane (Comparative Example 3) versus wavelength lambda (1) in units of nanometers for a sample a) loaded in N2 (dot line), b) loaded in N2,dried with 3A molecular sieves (solid line). Results below ~155 nm

30   exhibit saturation of the absorbance measurement.

DETAILED DESCRIPTION

The present invention provides a perfluoro-n-alkane liquid with a significantly high transparency at 157 nm that makes the perfluoro-n-alkane liquid of the invention surprisingly well-suited for use in imaging

5   applications in the wavelength range of ca. 150 – 165 nm, particularly at 157 nm, as well as in other applications requiring high transparency condensed phase optical components such as, for example, optical adhesive compositions, solvents for pellicle polymers, and index matching fluids. Of particular note is the suitability of the perfluoro-n-alkane in the

10   emerging field of immersion photolithography at 157 nm exposure wavelength wherein at least the target surface in a photolithographic apparatus such as is widely employed in the art of microcircuit fabrication is partially or wholly immersed in a liquid of high transparency but higher refractive index than air or other gaseous atmospheres.

15   As used herein, the terms "the perfluoro-n-alkane liquid of the invention" or "the perfluoro-n-alkane(s)" includes perfluoro-n-pentane, perfluoro-n-hexane, having the properties specified herein, and mixtures thereof. The terms "perfluoro-n-pentane" and "perfluoro-n-hexane" refer to the linear, unbranched isomers of perfluoropentane and -

20   perfluorohexane according to the usual chemical meaning thereof.

The terms "imaging" and "imaging applications", as used herein, mean processes whereby an image is formed on a substrate by a photoactivated process comprising emission of light or radiation from a light source in the wavelength range from 150 to 165 nm, preferably at

25   157nm, illumination of a surface over at least a portion thereof by said emitted light, and a liquid disposed between said light source and said surface in such manner that at least a portion of said emitted light illuminating said surface is caused to be transmitted through said liquid, said liquid selected from linear, unbranched perfluoro-n-pentane, linear,

30   unbranched perfluoro-n-hexane, and mixtures thereof. There is no limitation on the shape of the image formed, which can include a completely masked and a completely unmasked surface. The terms "light" and "radiation" are used herein interchangeably to refer to non-ionizing

electromagnetic radiation, particularly in the wavelength range from 150-165 nanometers, most particularly at 157 nm. The present invention does not encompass the use of ionizing radiation.

5　　　Concentrations where expressed as parts per million (ppm) refer to parts per million by weight on the basis of the total weight of the composition referred to.

The term "heart cut" as used herein in reference to fractional distillation refers to that portion of condensate that results during a fractional distillation when the temperature has reached a plateau
10　　indicating that the composition of the distillate is uniform.

The term "oxygen-minimized", which is used herein to refer to an atmosphere with which the perfluoro-n-alkane is to be handled and maintained, indicates that steps are taken to reduce the contamination of the purified liquid perfluoro-n-alkane by atmospheric oxygen. The most
15　　highly preferred oxygen-minimized atmosphere is one that contains oxygen below detectability; however the processes disclosed herein are operable at oxygen contents in the atmosphere such that the dissolved oxygen is < 10 ppm, preferably < 5 ppm, most preferably, <1 ppm. It is desirable to exclude oxygen because dissolved oxygen causes
20　　hydrocarbon immersion fluids to absorb light at 193 nm and because oxygen gradually degrades hydrocarbons chemically over time generating additional absorbing impurities. Pulling a vacuum above an immersion fluid can achieve substantially the same effect as filling the space with an inert gas and is an acceptable alternative to an inert gas. Using a vacuum is
25　　can be less desirable than using inert gas because a vacuum can pull air, including oxygen, into the container containing the fluid, and because having a vacuum over the fluid can make fluid transfer from one vessel to another more difficult.

The term "grease-free", as used herein, means that it is highly
30　　preferred that no grease is employed when assembling the cleaned parts of the system as is commonly done in the art of distillation, and that rigorous methods of cleaning such as are known in the art and commonly practiced when high purity is required are employed to minimize the

presence of any adventitious chemical contamination, including grease, of any of the parts of the system. One of skill in the art will appreciate that the term "grease-free" does mean that the invention is not operable should there be some small amount of grease contamination somewhere in the

5   system. To the extent that the system can be cleaned of all such contamination, the better will be the absorbance, but "grease-free" shall not be taken to mean the complete absence of grease in no matter how small a concentration.

High purity (>99%) commercially available perfluoro-n-pentane and
10   perfluoro-n-hexane have been found to exhibit an absorbance at 157 nm of ca. 15 cm^{-1} in the as-received state.

Provided in accord with the present invention is a composition consisting essentially of a liquid perfluoro-n-alkane characterized by an oxygen concentration of less than 10 ppm, a water concentration of less
15   than 10 ppm, and absorbance at 157 nm of 0.1 to 10 cm^{-1} said liquid perfluoro-n-alkane being selected from perfluoro-n-pentane, perfluoro-n-hexane, and mixtures thereof. In a preferred embodiment, said liquid perfluoro-n-alkane is characterized by an oxygen concentration of less than 5 ppm, a water concentration of less than 5 ppm, and an absorbance
20   at 157 nm of 0.1 to 2 cm^{-1}. In the most preferred embodiment, said liquid perfluoro-n-alkane is characterized by an oxygen concentration of less than 1 ppm, a water concentration of less than 5 ppm, and an absorbance at 157 nm of 0.1 to 1 cm^{-1}.

A low absorbance in combination with a refractive index in the
25   range of 1.30 to 1.35 at 157nm, a high degree of chemical inertness and stability, and its liquid state make the perfluoro-n-alkanes disclosed herein highly desirable for use in imaging applications in the wavelength range of 150-165 nm, particularly 157 nm.

Perfluoro-n-alkanes suitable for use according to the present
30   invention are liquid at room temperature and pressure and exhibit a highly desirable combination of high transparency and a desirably high refractive index that is relatively insensitive to temperature and pressure changes. Perfluoro-n-alkanes that are gaseous at room temperature and pressure

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can exhibit very low absorbance, but an undesirably low refractive index that is unstable because it is subject to large changes with small changes in pressure. Gaseous perflufo-n-alkanes can be inconvenient for practical use, requiring extensive measures for confinement and handling.

5   The liquid perfluoro-n-alkanes for use according to the present invention are highly suitable for employment as so-called immersion liquids in immersion photolithography at 157 nm. In immersion photolithography, described in detail hereinbelow, at least the target photoresist surface in the 157 nm photolithographic imaging system is

10   immersed in the perlluoro-n-alkane immersion liquid that has a desirably high transparency and high refractive index in order to effect high resolution lithographic imaging.

It is the surprising combination of properties exhibited by the perfluoro-n-alkanes disclosed herein that make it highly suitable for

15   immersion photolithography at 157 nm. The perfluroro-n-alkanes suitable for use according to the present invention are liquid at use temperature, and have an absorbance at 157 nm in the range of 0.1 to 10 cm^{-1}, preferably in the range of 0.1 to 2 cm^{-1}, most preferably in the range of 0.1 to 1 cm^{-1}. By contrast, higher homologs, while liquid and of high refractive

20   index, exhibit considerably higher absorbance at 157 nm. Thus, perfluoro-n-heptane is much less suitable, and perfluoro-n-octane, even in a purified form, clearly too absorbing for use at 157nm as shown in Table 1 and Comparative Example 3. Similarly, other isomers of perfluoropentane and perfluorohexane, including branched or cyclic isomers, can exhibit

25   excessively high absorbance at 157 nm. As shown in Table 1 herein, absorbance at 193 nm (or above) does not predict absorbance at 157 nm.

Perfluoro-n-pentane and perfluoro-n-hexane are available commercially at purities in excess of 99% from, respectively, SynQuest Laboratories, Inc., Alachua, Florida and the DuPont Company, Wilmington,

30   Delaware. Prior to the present invention, use of even the highly purified commercial grades of these materials for immersion photolithography at 157 nm exposure wavelength was not contemplated.

Certain organic impurities such as, for example, acid fluorides and olefins are orders of magnitude more absorbing than other organic impurities such as perfluoroheptane. For example, for use according to the present invention, the perfluoroalkanes can be contaminated by a

5   percent or two of perfluoroheptane, or an even higher percentage of perfluorobutane, which is quite transparent though of high vapor pressure and low refractive index. On the other hand, the perfluoroalkanes for use according to the present invention are preferably uncontaminated by, or contaminated by less than 0.1% of, much more highly absorbing

10   contaminants such as chlorinated fluorocarbons, olefins, including fluoroolefins, and carbonyls, including fluorocarbonyls. For some contaminants, concentration as low as 0.0001% can be detrimental.

In the practice of the present invention, it may be useful to analyze the as received perfluoro-n-pentane or perfluoro-n-hexane by a gas

15   chromatography - mass-spectroscopy (GC-MS) in combination with NMR to determine what organic contaminants are present, and, what purification steps are indicated. From a practical standpoint, it may be more productive to omit the cost-intensive analysis, and simply put all aliquots of the perfluoroalkane through the same purification steps. Purification can

20   include fractional distillation, sparging, freeze-thaw cycling, zone refining, and treatment with absorbents such as silica, molecular sieves of various pore sizes, carbon, silica gel, or mixtures thereof. Suitable molecular sieves include size 3A, 4A, and 5A zeolite molecular sieves.

In a highly preferred embodiment of the invention, a perfluoro-n-

25   alkane exhibits absorbance at 157 nm in the range of 0.1 to 1 cm^{-1}. It will be appreciated by one of skill in the art that at purity levels required to achieve such absorbance at 157 nm, the most sensitive measurement of contamination is the spectroscopic absorption itself. Thus, the best way to tell that the most important impurities have been removed may be to

30   measure the absorbance. Absorbance below 1 cm^{-1} is by far the most sensitive available indicator of purity. It is believed that, prior to the present invention, it was not known that such levels of absorbance could be achieved in the perfluoro-n-alkanes.

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It is found that certain perfluoro-n-alkanes, as disclosed herein, as received or as synthesized, exhibit an oxygen content generally in the range of 90 ppm. Perfluor-n-alkanes, as received or as synthesized, generally contain trace contaminants, possibly including moisture, that can

5   be removed by exposing the fluid to absorbents such as molecular sieves or silica gel. It has been surprisingly found that the transparency of the perfluoro-n-alkanes, having been purified according to the processes disclosed herein, can be improved by as much as two orders of magnitude.

10   Known methods for performing extractions of particular types of contaminants can be used in the practice of the present invention, but such methods are preferably carried out under such clean conditions to avoid further contamination.

In order to achieve the highly desirable low absorbance at 157 nm

15   in the perfluoro-n-alkanes, it is desirable to extract not only highly absorbing organic impurities, but also environmental contaminants such as oxygen and water, most particularly oxygen, and then take strenuous efforts to avoid recontamination. It is found in the practice of the present invention that oxygen, because of its ubiquity, is the most pernicious

20   contaminant because small concentrations in the perfluoro-n-alkanes can cause significant degradation of transparency – i.e., increased absorbance at 157nm.

Preferred is to perform fractional distillation followed by mixing the heart cut of the condensate thereof with a solid absorbent followed by

25   filtration just prior to use, all conducted in an oxygen-minimized atmosphere such as nitrogen, helium or argon. Finely dispersed solid absorbents can be suspended in the perfluoro-n-alkane and then filtered out. Types 3A, 4A, and 5A molecular sieves are preferred because their cavities are of a size that favor the selective absorption of water and other

30   trace contaminants from organic vapors and fluids. Silica gel is also suitable. Most preferably a mixture of absorbents is employed.

There are no limitations on the methods of absorption that can be employed to achieve the desired state of purity, provided that the method

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employed does not introduce more undesirable contamination than it removes, and that the method not cause significant degradation of the compound being purified. Thus, any method known to one of skill in the art for absorbing contaminants from organic liquids is suitable.

5   The most preferred method for preparing the most preferred perfluoro-n-alkane suitable for use according to the present invention is to combine fractional distillation with contacting the condensate thereof with absorbents, preferably mixed absorbents, all in an oxygen-minimized atmosphere.

10   In a preferred embodiment, first the as-received compound, which is generally of a purity greater than 99%, is subject to fractional distillation in the cleanest possible, grease-free distillation apparatus. The heart cut of the condensate thus produced is then mixed in the liquid state with a mixture of absorbents, such as, for example, silica gel, 3A, and 5A zeolite

15   molecular sieves. Activated carbons are less preferred as absorbents. The absorbents are subject to oxidation at a temperature high enough to remove substantially all water and oxidize any organic contaminants. The absorbent is then cooled and sealed in an oxygen-minimized atmosphere such as a nitrogen atmosphere. Other oxygen-minimized atmospheres

20   known to those skilled in the art can be used. It has been found suitable in the practice of the invention to heat the absorbents at 500°C for two hours in an oxygen containing atmosphere followed by cooling to 100°C under a slow flow of moisture and oxygen free nitrogen. The N_2 flow is stopped and the system put under vacuum while the remaining parts of the

25   apparatus are dried with a heat gun. The system is cooled to room temperature in a sealed chamber prior to use. All subsequent handling of the thus purified perfluoro-n-alkane is then performed in an oxygen-minimized, preferably nitrogen, atmosphere. This includes the use thereof in immersion photolithography, which is advisedly performed in an oxygen-

30   minimized, preferably nitrogen, atmosphere.

It is highly preferred that the distillation be performed in the cleanest, least contaminated apparatus that is practical. It is particularly desirable to exclude oxygen and any adventitious or systemic organic

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contaminants. It has been found that employment of grease, including fluorinated greases, such as are commonly employed in distillation and vacuum systems to provide improved sealing and easier part removal, can contaminate the distillate herein sufficiently to actually degrade the

5   absorbance. It is therefore highly preferred to perform the distillation in what is herein designated a "grease-free" distillation system.

In addition to the process of fractional distillation in combination with contacting the liquid condensate thereof with absorbents in an oxygen-minimized atmosphere, other methods known for removing moisture are

10   suitable for the practice of the present invention. Examples of such methods include exposing to a desiccated purge gas such as in a recirculating air oven having desiccant beds; refluxing in the presence of a desiccated purge gas, sparging with a purge gas, preferably an inert gas such as nitrogen or argon; contacting with a desiccant such as molecular

15   sieves; vaporization of the liquid perfluoro-n-alkane liquid, passage of the vapor over a desiccant such as molecular sieves, followed by condensation (freeze-thaw cycles, usually including a step for evacuation of the closed vessel after recondensation of the vapor); or contacting with chemical desiccants such as isocyanates. In the case of contact with a

20   desiccant it may be necessary to add a separation step upon completion of the extraction step.

Oxygen contamination not only degrades transparency at 157 nm but is also a source of photochemical instability at the high energies of VUV radiation. Oxygen is known to be closely associated with

25   degradation reactions in many materials. The technique of sparging with an inert gas, preferably nitrogen or argon, is effective for removing oxygen from the perfluoro-n-alkanes. Examples of other methods suitable for removing oxygen include heating in an oven under vacuum, or under an oxygen free purge gas, contacting with an oxygen scavenger, repeated

30   cycles of freezing, pulling a high vacuum and thawing, and vacuum distillation and fractional distillation. It has been found that simply handling and maintaining the perfluoro-n-alkane in an oxygen-minimized atmosphere can result in considerable reduction in oxygen concentration.

Furthermore, fractional distillation under a nitrogen flow appears to be effective at decreasing oxygen contamination since evolved oxygen will not recondense.

5   There are no limitations on the methods of extracting oxygen that can be employed to achieve the desired oxygen concentration, provided that the method employed not introduce more undesirable contamination than it removes, and that the method not cause significant degradation of the compound being purified. Thus, any method known to one of skill in the art for extracting oxygen from organic liquids is suitable.

10   Sparging is a suitable method for practicing the process of the invention, particularly for the removal of oxygen. One method for sparging found effective in the practice of the invention is as follows: A glove box is supplied with dry, low-oxygen-content nitrogen such as 99.998% purity, or greater, nitrogen available as a cylinder gas, for example, from Matheson, 15 or obtained by the boil-off of liquid nitrogen. A liquid aliquot of about 10 ml is placed in a 20 ml glass scintillation vial. The aliquot is transferred into the nitrogen purged dry box. The vial is secured flat on the work surface, the plastic cap is removed from the vial, a disposable glass pipette lowered into the solvent and then nitrogen delivered via the pipette from 20 the same dry, low-oxygen source as the glove box. Flow rate is adjusted to maintain vigorous bubbling of solvent short of causing the solvent to splash out of the vial. Vigorous sparging is continued for 30-60 seconds, long enough to significantly decrease oxygen content and possibly water content without major loss of solvent to evaporation.

25   An alternative method for purifying the perfluoro-n-alkane is bulb-to-bulb distillation through a bed of 3 A molecular sieves. For example, two flasks are connected by a tube containing 3A molecular sieves preheated as described above. One of the flasks is then partially filled with the fluid that is to be purified, e.g.,, perfluoro-n-hexane, and the system resealed. 30 The perfluoro-n-hexane is subjected to three freeze/thaw cycles to remove oxygen dissolved in the perfluoro-n-hexane. The system is then thoroughly evacuated after refreezing the perfluoro-n-hexane with liquid nitrogen. The system is sealed under vacuum and the liquid nitrogen cooling bath

transferred from the flask containing the perfluoro-n-hexane to the empty flask. As the perfluoro-n-hexane warms towards room temperature it distills through the bed of 3A molecular sieves to the chilled flask. Once distillation is complete the vacuum is relieved with moisture and oxygen

5   free nitrogen, the perfluoro-n-hexane allowed to warm to room temperature, and the perfluoro-n-hexane flask then valved off for subsequent use.

As used herein, the terms "desiccated" as in "desiccated atmosphere" or "desiccated purge gas" mean that the atmosphere or

10   purge gas is sufficiently low in moisture content that it can function effectively to extract moisture from the perfluoro-n-alkane. Preferably, a desiccated purge gas or desiccated atmosphere will have been previously subject to a drying step prior to its use for extraction of moisture.

In the practice of the present invention, extraction of any one

15   photochemically active species is beneficial whether or not any other photochemically active species present is extracted.

The pefluoro-n-alkanes disclosed herein are highly suitable for use in processes that use a light source emitting light in the wavelength range from 155 to 160 nm, a surface illuminated over at least a portion thereof by

20   said emitted light, and the perfluoro-n-alkane(s) disposed between the light source and the surface such that at least a portion of the emitted light illuminating the surface is caused to be transmitted through the liquid. The liquid can comprise perfluoro-n-pentane, perfluoro-n-hexane, or a mixture thereof.

25   Preferably the light source emits light at 157 nm. More preferably the light source is a laser. Most preferably the light source is an F_2 excimer laser emitting light at 157 nm.

Preferably the surface is a photoresist surface. More preferably the photoresist surface resides on a silicon wafer. Preferably the illumination

30   is an imagewise exposure of the preferred photoresist surface. Preferably the photoresist surface is immersed in the liquid. Preferably all of said emitted light is employed to illuminate said immersed surface. The preferred embodiment wherein a photoresist surface immersed in said

liquid is subject to image-wise exposure by said light source is the preferred immersion photolithography embodiment of the present invention.

One use for which the perfluoro-n-alkanes are particularly well-suited is in immersion photolithography at 157 nm as described by Switkes et al, *op.cit.*, wherein at least the photoresist surface target is immersed in the optically transparent, chemically inert, high refractive index perfluoro-n-alkane immersion liquid. Among the requirements for an immersion liquid disclosed by Switkes are that it be transparent enough to allow a working distance of at least tens of micrometers and that it have high radiation durability at 157 nm. The combination of high transparency and high radiation durability of the perfluoro-n-alkane immersion liquids of the present invention makes them particularly well-suited for immersion photolithography at 157 nm exposure wavelength applications at 157 nm.

Additional desirable properties for a suitable immersion liquid are that it be chemically and physically compatible with the materials used in the system. In immersion photolithography at 157 nm exposure wavelength, the immersion fluid is in contact with a photoresist polymer. An immersion fluid preferably does not dissolve the photoresist, interfere with latent image formation in the photoresist under 157 nm exposure, or interfere with subsequent development of the photoimaged photoresist in a developer solution. In addition the immersion fluid preferably has a low enough volatility that it does not require a pressure vessel for containment and is easily removed for reprocessing prior to post exposure baking, and development.

Three types of imagewise exposure are contemplated to fall within the framework of immersion photolithography at 157 nm exposure wavelength at 157 nm. These are contact, proximity and projection immersion photolithography at 157 nm exposure wavelength. In projection immersion photolithography at 157 nm exposure wavelength, the index of refraction of the fluid can be considered to produce a reduced wavelength of the lithographic light in the immersion fluid, given by $\lambda_{immersion\ fluid} = \lambda_{vacuum} / n_{immersion\ fluid}$ where λ is the wavelength in the immersion fluid or

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vacuum respectively and n is the index of refraction of the immersion fluid. This effective reduction of the optical wavelength in the immersion fluid allows for an improvement in the ultimate resolution that can be printed using immersion photolithography at 157 nm exposure wavelength.

5   In the case of contact and proximity immersion photolithography at 157 nm exposure wavelength, the wavelength of the lithographic light in the fluid is the same as for projection immersion photolithography at 157 nm exposure wavelength, but the feature sizes printed are dictated by the contact or proximity mask used. In contact or proximity immersion

10   photolithography at 157 nm exposure wavelength the primary purpose of the perfluoro-n-alkane immersion liquid is to protect the imaged surface. Additionally, contact or proximity immersion photolithography at 157 nm exposure wavelength are useful screening methods for determining the usefulness of a candidate liquid for the more complex and expensive but

15   more preferred projection method.

157 nm radiation from, for example, a F_2 excimer laser, is transmitted through a photomask, typically comprising a chrome metal circuit patterned on glass by electron beam imaging, forming an image of the circuit pattern on a photoresist. Numerous materials for use as

20   photoresists are well known in the art and are in widespread commercial use. All such materials are suitable for the practice of the present invention so long as they are functional at 157 nm and are largely insoluble in the immersion fluid. Suitable photoresist compositions are described in Introduction to Microlithography, Second Edition by L. F.

25   Thompson, C. G. Willson, and M. J. Bowden, American Chemical Society, Washington, DC, 1994.

One of skill in the art will appreciate that the source of the 157 nm radiation, or of any radiation in the wavelength range of 150-165 nm, is not critical to the practice of the invention. F_2 excimer lasers are convenient,

30   controllable, high intensity sources of 157 nm radiation and are preferred.

An example of a photolithographic process is depicted in Figures 13-15. Figure 13 shows a complete system disposed on an optical table (6) with air support legs to minimize vibrations in the photolithographic

exposure chamber. A Scientech power meter (1) is used to read the
energy of the 157nm laser pulses emitted by an F2 excimer laser (9). In
the particular embodiment depicted in Figure 13, the photolithographic
exposure chamber is a conventional laboratory nitrogen flushed dry-box
5   (2) adapted for use in the apparatus therein depicted. The 157 nm laser
light is introduced into the dry box through one of the gloved access ports
(8). A Thermox oxygen analyzer (3) is used to monitor the oxygen content
in the dry box, and to indicate when oxygen concentration has decreased
to acceptable levels after introduction of new samples. Upon introduction
10   into the dry box chamber, the laser beam is reflected downwards by a
mirror (4) to the photoresist coated silicon wafer (5). The photoresist
coated wafer is immersed to a depth of ca. 1 mm in a perfluoro-n-alkane
suitable for use in the present invention contained in a glass dish . The
whole dish can be translated under the laser beam to allow sequential
15   exposures of different portions of the wafer, with differing exposure doses.

     Figure 14 shows more details of the optical exposure system of
Figure 13. The pulsed laser beam from the Excimer laser enters the dry
box (3) at (6), and is incident on a CaF2 beam splitter (5), that reflects a
small portion of the laser energy, down to a power meter head (4), so as to
20   measure the laser's energy per pulse. The majority of the laser beam
continues through the beam splitter (5) and is then incident on a dichroic
mirror (1), designed for use at a 45o angle of incidence of 157 nm light,
such that the laser beam is redirected into the vertical direction, downward
towards the photomask covered, photoresist coated silicon wafer (2).

25   Figure 15 shows the wafer exposure stage, where the laser beam
from the excimer laser, passes through the CaF2 window (2) on the fixed
cover plate (1) of the exposure stage. The glass petri dish (3) moves
under the glass cover plate using the translation stage (7) of Figure 13, so
as to permit the sequential exposures, at various exposure doses. (4) is
30   the inside of the glove box,. (5) is the silicon wafer, which has been
coated with a photosensitive photoresist polymer (6) as discussed in more
detail below. Depicted in Figure 15 is an embodiment of the invention
known as contact photolithography at 157 nm exposure wavelength

wherein a photomask (7) is placed on the surface of the photoresist polymer layer. Figure 15B depicts the same set-up but without the immersion fluid; Figure 15B is not an embodiment of the present invention. It is found in the practice of the invention that when the
5   photomask is small and light, as for example the grids used in the specific embodiments herein, it is convenient to introduce the immersion fluid first and then to position the photomasks in the fluid and on the surface of the photoresist coated silicon wafer.

The photomask may be offset from the surface of the photoresist by
10   a distance of ca. 1 mm. The preferred method is so called projection photolithography at 157 nm exposure wavelength, wherein the photomask is disposed at some convenient location in the optical path, and the image is projected via a lens system, typically known as a projection lens, onto the photoresist. The projection system provides the highest resolution of
15   the various embodiments of the present invention.

In projection photolithography, the output element of the projection lens – that end of the lens system which is closest to the photoresist surface - is disposed within the perfluoro-n-alkane immersion liquid at a distance of about 0.5 –5 mm from the photoresist surface, which is
20   immersed in the immersion liquid. This method provides the highly desirable benefit of effectively shortening the wavelength of the incident light, thereby increasing the resolution of the technique over that which can be attained in a gaseous atmosphere such as air or nitrogen.

The thickness of the layer of immersion fluid is determined by the
25   details of the imaging system being developed or used. For example in contact photolithography at 157 nm exposure wavelength a suitable thickness of the perfluoro-n-alkane immersion liquid is 1mm. A 1 mm thickness may also be suitable for scanning or stepping the wafer under a projection lens, while maintaining sufficient distance between the output
30   element of the projection lens and the wafer. One of skill in the art will appreciate that as the immersion fluid thickness is increased attenuation of the light will also increase, but tolerances in regard to the mechanics of stepping and scanning may become easier. Thinner immersion liquid

layers may permit higher light exposure levels but the tolerances required
for achieving scanning and/or stepping the wafer at high speed and with
high accuracy may become excessively demanding.

5   The perfluoro-n-alkane immersion liquids of the present invention
present a highly desirable combination of properties. They are easily
handled, relatively low viscosity liquids at room temperature. They exhibit
desirably low absorbance at 157 nm: in preferred embodiments, an
absorbance of less than 2 cm^{-1}, in most preferred embodiments, less than
0.2cm^{-1}. In highly preferred embodiments, the perfluoro-n-alkanes exhibit

10   a desirably high refractive index of about 1.315. This compares to the
much higher absorbance of higher homologs such as highly purified
perflouro-n-octane of ca. 54 cm^{-1} on the one hand, or lower, gaseous
homologs such as perfluorobutane which exhibit very low absorbance but
refractive indices which depend very sensitively upon pressure and

15   temperature, and which are much lower.

The perfluoro-n-alkane immersion liquids provide a high degree of
flexibility in system design, reducing the need to trade-off between the
thickness of the immersion layer and mechanical design.

Both positive working photoresists and negative working

20   photoresists are suitable for use in immersion photolithography with the
perfluoro-n-alkanes. A positive working photoresist is a resist where the
exposure to light, leads to a change in the dissolution behavior of the
polymer, such that after development, the exposed regions of the
photoresist dissolve away into the developer. In negative working

25   photoresists, the exposed regions stay, while the unexposed regions
dissolve in the developer. The photoresist, when exposed to light, forms
what is called a latent image. In a typical method, a chemically amplified,
positive tone resist that contains a photoacid generator, or PAG, is
employed. The photoresist layer comprising the latent image is then

30   subjected to a post exposure bake (PEB) step, whereby the photoacid
generator produces photoacid, which then catalytically breaks down the
backbone of the photoresist. After the PEB step, the photoresist coated
wafer is then put into an aqueous base developer, such as a 0.26 Normal

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TMAH developer, whereby the exposed regions of the polymer film are developed away, and the patterned photoresist is observed.

In characterizing the behavior of a photoresist used in a photolithographic process, two useful exposure parameters employed in

5   the art are E0 the exposure dose to clear the photoresist from large areas that are not patterned, and E1, which is the dose required to get a patterned area of the photoresist, to produce features of the desired sizes. E0 is sometimes called the clearing dose, for clearing the photoresist, and E1 is the sizing dose, for achieving features of the correct size.

10   While there is no particular limitation on the thickness of the photoresist layer, in typical practice the photoresist coating is 150 nm to 200 nm in thickness on a silicon wafer substrate. The thickness is determined by the desired minimum feature sizes to be printed. For the purpose of illustration of this concept, but in no way limiting on the scope

15   of application of the process of the invention, using an aspect ratio of 3 - 4, a typical value in the semiconductor art, if the desired features are 65 nm in width, the film thickness should be ~ 195nm. In general, the thicker the photoresist layer, the better resistance to dry etch processes in subsequent processing of the patterned photoresist layer.

20   In a complete semiconductor manufacturing process, the photolithographic imaging and development of a photoresist layer, is performed many times in sequence, with a series of photomask patterns, and with various etch and deposition processes done between the sequential photolithographic steps.

25   The perfluoro-n-alkane can be employed in a variety of applications in addition to as an immersion liquid in photolithography. Applications include those in which the perfluoro-n-alkane is disposed between a 157 nm light source and a target. The perfluoro-n-alkane can be employed neat, as in liquid lenses, index matching fluid, and the like, or can be an

30   ingredient of a mixture or a diluent such as a solvent for polymers in spin-coating operations , a plasticizer in a polymeric film, or a solvent in an adhesive formulation. In another embodiment, the perfluoro-n-alkanes are useful in the optical inspection of patterned or unpatterned objects such as

semiconductor wafers, where small size defects of varying optical properties are to be detected. The use of the perfluoro-n-alkanes as immersion fluids for immersion inspection enables both higher resolution imaging in the inspection, and also reduce optical scattering from the

5   topography of the sample, permitting the inspection of, for example deep holes which may have defects such as particulate debris present.

In still further embodiments, the perfluoro-n-alkanes are useful in the fabrication of sheets, layers, coatings, and films used in lenses, light guides, anti-reflective coatings and layers, windows, protective coatings,

10   and glues suitable for use in 157 nm photolithography.

The perfluoro-n-alkanes can also be used as elements in a compound lens designed to reduce chromatic aberrations. Heretofore, it is believed that only CaF_2 and hydroxyl free silica have been viewed as having sufficient transparency at 157 nm to be used in transmissive

15   focusing elements. It is also commonly known (e.g., see R. Kingslake, Academic Press, Inc., 1978, Lens Design Fundamentals, p. 77) that by using a second material of different refractive index and dispersion, an achromatic lens can be created. By using the perfluoro-n-alkanes of the present invention in conjunction with CaF_2, it is expected that an

20   achromatic lens can be constructed.

The perfluoro-n-alkanes are suitable for any application that uses a highly transparent liquid in the wavelength range of 150 to 165 nm.

The present invention is further described but not limited to the following specific embodiments.

25   EXAMPLES

Water concentration was determined according to the Karl Fischer method commonly employed in the art. The effect of drying over molecular sieves of the preferred compositions of the invention is indicated in Table 1.

30   The transmission based absorbance measurements of the fluid samples were made using a Harrick Scientific Corp. (Harrick Scientific Corporation 88 Broadway Ossining, NY) Demountable Liquid Cell model

DLC-M13 as shown in Figure 3. The DLC-M13 was mounted in a VUV-Vase model VU-302 spectroscopic ellipsometer, which was capable of performing transmission measurements (J.A. Woollam Co., Inc. Lincoln, NE). The liquid specimen to be tested was held in a cell formed between
5   parallel CaF$_2$ windows by insertion of a Teflon® ring between the windows. Teflon® rings of 6, 25, 100, 500, 920, 2200, 3000 and 4000 micrometer thicknesses were used, providing multiple optical path lengths through aliquots of the same sample. While charging the cell, care was taken to avoid bubbles in the 8 mm diameter window aperture.

10   The optical absorbance, A (cm^{-1}), per centimeter of specimen thickness as defined in Equation 1, is defined for purposes herein as the base 10 logarithm of the ratio of the transmission of the CaF$_2$ windows at the test wavelength divided by the transmission at that wavelength of the test sample (windows plus experimental specimen) divided by the
15   thickness (t) of the test specimen -- in the case of the experiments reported herein, either 6, 25, 100, 500, 920, 2200, 3000 or 4000 micrometers, as discussed hereinabove.

$$\text{Equation 1.} \quad A(cm^{-1}) = A/cm = \frac{Log_{10}\left[T_{substrate}/T_{sample}\right]}{t}$$

20

To eliminate the effect of multiple reflections in the case of the liquid samples employed herein, absorbance was determined using the relative change in the transmission of multiple liquid filled Harrick cells with differing cell spacer thicknesses. For example for two different cell
25   thicknesses, the spectral transmission was measured at both cell thicknesses (t_1 and t_2) and the incremental decrease in transmission (T_1 and T_2) with the increase in the sample's optical path length provides the optical absorbance / centimeter using Equation 2.

30    $$\text{Equation 2.} \quad A/cm = \frac{\log_{10}(T_1) - \log_{10}(T_2)}{t_2 - t_1}$$

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We generalized this relative transmission method for absorbance determination from multiple optical path lengths in the sample so as to achieve better accuracy in determining the optical absorbance per centimeter of these materials. We used up to 5 different optical path lengths, spanning from 6 to 4400 micrometer cell thicknesses. In this case we measured the transmission T_n (in general) as a function of thickness t_n for the cells of various thicknesses.

$$T_1(\lambda) = T_0(\lambda)e^{-\alpha(\lambda)t_1}$$
$$T_2(\lambda) = T_0(\lambda)e^{-\alpha(\lambda)t_2}$$
$$T_3(\lambda) = T_0(\lambda)e^{-\alpha(\lambda)t_3}$$
$$...$$
$$T_n(\lambda) = T_0(\lambda)e^{-\alpha(\lambda)t_n}$$

Then taking logarithm of all equations gives

$$\ln T_1(\lambda) = \ln T_0(\lambda) - \alpha(\lambda)t_1$$
$$\ln T_2(\lambda) = \ln T_0(\lambda) - \alpha(\lambda)t_2$$
$$\ln T_3(\lambda) = \ln T_0(\lambda) - \alpha(\lambda)t_3$$
$$....$$
$$\ln T_n(\lambda) = \ln T_0(\lambda) - \alpha(\lambda)t_n$$

This is a set of N equations for the linear system $y_i = ax_i + b$, where $y_i \equiv \ln T_i(\lambda)$, $a \equiv -\alpha(\lambda)$, $b \equiv \ln T_0(\lambda)$, and $x_i \equiv t_i$.

We used linear algebra to simultaneously solve this system of linear equations by a least squares method for the absorbance/centimeter of the samples. The solutions were done both for the case where the errors of measurement for all observations were independent of i, (homoscedastic), the equations were solved by a least-squares method and for the case where the errors of measurement were dependent on i, (heteroscedastic), the equations were solved by a weighted least-squares method.

As an example for the homoscedastic case the equations we solved are:

$$\frac{\partial}{\partial \alpha} \sum \left(\ln T_i(\lambda) + \alpha(\lambda)t_i - b(\lambda) \right)^2 = 0$$

$$\frac{\partial}{\partial b}\sum\left(\ln T_i(\lambda) + \alpha(\lambda)t_i - b(\lambda)\right)^2 = 0$$

And the solutions are:

$$\alpha(\lambda) = \frac{\sum t_i \sum \ln T_i(\lambda) - N\sum t_i \ln T_i(\lambda)}{N\sum t_i^2 - \sum t_i \sum t_i}$$

$$b(\lambda) = \frac{\sum \ln T_i(\lambda)\sum t_i^2 - \sum t_i \ln T_i(\lambda)\sum t_i}{N\sum t_i^2 - \sum t_i \sum t_i}$$

From this analysis of multiple transmission measurements of the material at multiple cell thicknesses we were able to determine the absorbance/centimeter of the material.

Harrick Liquid Cell Procedures

For the purpose of measuring the spectral transmission of fluids as candidates for Immersion Fluids to be used in MicroLithographic Processing, we used a Harrick DLC-M13 demountable liquid cell. The cell had a 8mm aperture, which included (2) 13mm diameter x 2mm thick CaF2 windows, o-ring seals, (2) Luer Lock fittings for loading sample, assorted Teflon spacer thick nesses from 6um to 4000um. The cell was disassembled for cleaning.

Harrick Cell Cleaning and Assembly Procedure:

Prior to use, and after each sample run, the cell was flushed with Vertrel® XF, (as a cleaning solvent), through both Luer Lock fittings using a 1ml BD glass syringe, then blown dry using clean house nitrogen which is generated by boil-off of liquid nitrogen. The (2) CaF2 windows and the selected thickness Teflon spacers were placed into a 20ml vial containing Vertrel® XF, (capped), then put into an ultrasonic bath for, 30-60 seconds. The CaF2 windows and spacers were removed form the cleaning vial, given a final rub with a Q-tip moistened with Vertrel® XF then dried with air from a puffer bulb. The cell was then assembled by placing an o-ring into the internal base of the cell, then placing one of the CaF2 windows into the cell, followed by the Teflon spacers, then the second or top CaF2 window, then putting the top o-ring in on the CaF2, place the compression ring onto

this assembly then hand tightened the compression nut onto the cell. The complete cleaning and assembly was done in air, in the lab hood.

Loading the Harrick Cell in Air...(Lab Hood)

5   Using a clean, fully assembled cell, approximately 0.5ml of the sample liquid was transferred from its container using a clean 1ml BD glass syringe, the syringe was then Luer Locked into the cell and the plunger was gently pushed up to fill the cell. The cell was filled until the liquid meniscus began to exit the top Luer Lock fitting on the cell. No trapped bubbles were permitted to reside in the cell aperture, then the top

10   Luer Lock fitting was capped with the Teflon plug supplied, and the cell was inverted with the syringe still attached. The syringe was twisted off, the thus exposed fitting was capped with another Teflon plug. The sample so prepared was ready for processing.

Loading the Harrick Cell in Nitrogen...(Nitrogen Dry Box)

15   A cleaned, assembled cell, with Teflon plugs (separate, not inserted), a clean 1ml BD syringe and the selected sample material were placed into the N2 dry box anti-chamber. This chamber was continually purged with house nitrogen until the Oxygen meter on the dry box read 10ppm O2 -- approximately 30minutes. The equipment was then

20   transferred into the dry-box proper.

           The sample bottle was opened and approximately 0.5ml of the sample was transferred from its container using a clean 1ml BD glass syringe, the syringe was Luer Locked into the cell and the syringe plunger gently pushed up to fill the cell. The cell was filled until the liquid meniscus

25   began to exit the top Luer Lock fitting on the cell. No trapped bubbles were permitted to reside in the cell aperture, then the top Luer Lock fitting was capped with the Teflon plug supplied, and the cell was inverted with the syringe still attached. The syringe was twisted off, the thus exposed fitting was capped with another Teflon plug. The sample so prepared was ready

30   for processing.

27

Loading a 3A dried sample into the Harrick Cell in Nitrogen...(Nitrogen Dry Box)

A cleaned, assembled cell, with Teflon plugs (separate; not inserted), a clean 1ml BD syringe and the selected sample that had been dried over 3A molecular sieves, still in the sample bottle, were placed in the dry box described above in the manner described.

The sample bottle was opened and the liquid poured into a clean 15ml BD syringe with a 0.45 micrometer PTFE Lure Lock filter. Using the syringe, the liquid was transferred through the filter into a clean, dry 20ml vial. Approximately 0.5ml of the thus filtered sample was transferred into the cell using a clean 1ml BD glass syringe the plunger of which was gently pushed to fill the cell. The cell was filled and secured as described above.

Absorbance/centimeter determination

For the purpose of the examples herein below, the absorbance of a material was determined using the relative transmission methods described above, for various cell thicknesses.

As in all experimental measurements, the accuracy of the measured values was a function of the sample and measurement apparatus. The inherent sensitivity of spectral transmission and absorbance measurements was affected by the optical path length of the sample, and the transmission drop that occurred as light passed through the sample in the measurement. As the transmission drop decreased, the accuracy of the absorbance measurement decreased. A transmission difference of ~ 0.1 % was near the limit of the measurement method. In such a case, a thicker sample, with a longer path length, was required to keep the measured transmission drop larger than the instrument's sensitivity.

Index of refraction determination

The index of refraction of the material and its temperature coefficient was determined using one of two methods either the minimum deviation prism method on the VUV-vase instrument (see for example John H. Burnett, Rajeev Gupta, and Ulf Griesmann, "Absolute refractive

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indices and thermal coefficients of CaF2, SrF2, BaF2, and LiF near 157
nm" , Appl. Opt. 41, 2508-2513 (2002)) or using the VUV Hilger-Chance
Refractometer (see for example John H. Burnett, Simon G. Kaplan, John
Fuller, Roger H French, Michael F. Lemon, Measurement of the Index

5   Properties of Fluids for 193 nm and 157 nm Immersion Photolithography at
157 nm exposure wavelength, International Sematech (ISMT) 2004
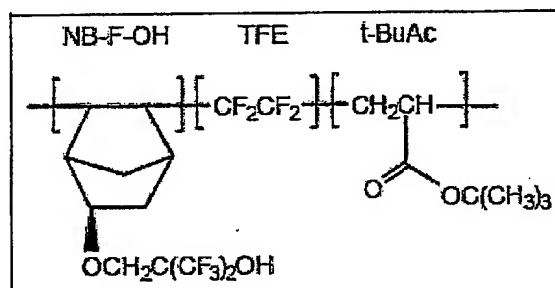Immersion Photolithography at 157 nm exposure wavelength Workshop,
Los Angeles CA, 1-27-04.).

<u>157 nm Contact Photolithography at 157 nm exposure wavelength</u>

10   This demonstrates the ability of the perfluoro-n-alkanes to
lithographically print using Contact Photolithography at 157 nm exposure
wavelength at a 157 nm Lithographic wavelength, with and without the
presence of an immersion fluid. The procedures for Contact
Photolithography at 157 nm exposure wavelength are as follows:

15   Preparing Silicon Wafers/Photoresist for Lithographic Processing
        Four inch diameter Silicon wafers with native oxide were primed
with a 0.5 nm thick HMDS coating to enhance uniformity and adhesion of
the photoresist film onto the wafer.
        A Dupont Terploymer 157nm Photoresist was spin coated onto

20   each Silicon wafer. The 157 nm photoresist used here consists of a
polymer consisting of a fluorinated terpolymer resins composed of 1)
tetrafluoroethylene (TFE), 2) a norbornene fluoroalcohol (NBFOH), and 3)
t-butyl acrylate (t-BA).
        These polymers were prepared by free radical solution

25   polymerizations using a standard initiator (peroxydicarbonate) and a
hydrofluorocarbon solvent, as described in.   A. E. Feiring, J. Feldman,

F. L. Schadt III, K. W. Leffew, F. C. Zumsteg, M. K. Crawford, R. H. French. R. C. Wheland, V. A. Petrov, W. B. Farnham, "Design of Very Transparent Fluoropolymer Resists for Semiconductor Manufacture at 157 nm" Journal of Fluorine Chemistry, 122, 11-16, (2003).

5   The photoresist used in these examples was formulated with a polymer whose composition is 33% TFE, 43% NBFOH and 24% t-BA, and using standard onium photoacid generators (5 wt% of triphenylsulfonium nonaflate, TPS-Nf), and a base (10 mole% of the PAG loading tetrabutylammonium lactate, TBALac), and a standard solvent (2-

10   heptanone). Details of the resist formulation and processing are in M. K. Crawford, W. B. Farnham, A. E. Feiring, J. Feldman, R. H. French, K. W. Leffew, V. A. Petrov, W. Qiu, F. L. Schadt III, H.V. Tran, R. C. Wheland, F. C. Zumsteg, "Single Layer Fluoropolymer Resists for 157 nm Photolithography at 157 nm exposure wavelength", Advances in Resist

15   Technology and Processing XVIII , SPIE Vol. 5039, (2003) and also A. E. Feiring, J. Feldman, F. L. Schadt III, K. W. Leffew, F. C. Zumsteg, M. K. Crawford, R. H. French. R. C. Wheland, V. A. Petrov, W. B. Farnham, "Design of Very Transparent Fluoropolymer Resists for Semiconductor Manufacture at 157 nm" Journal of Fluorine Chemistry, 122, 11-16, (2003).

20   Approximately 1 ml of Terpolymer resist was dispensed onto the wafer, centered on the spin coater chuck, through a 0.45 micron polytetrafluoroethylene syringe filter. The wafer was spun at 2200rpm for 60 seconds then a Post Apply Bake of the resist was done at 125 °C for 60seconds. The photoresist films were visually inspected and film

25   thickness of each film measured using a FilMetrics film thickness instrument (San Diego, CA, 92123). Film thicknesses were typically 2000A +/- 100A. Handling of all samples having unexposed Terpolymer Photoresist was done under yellow lighting.

157 nm Contact Lithographic Exposures

30   A Lambda-Physik Optex Excimer Laser (Ft. Lauderdale, FL 33309) at 157nm was used to determine the exposure dose necessary to obtain E0, (Open Frame Exposure Dose), and E1 , (Printing Exposure Dose with contact mask), in both Dry, (without immersion fluid), and Wet, (immersion

fluid). All exposures were undertaken in the nitrogen purged glove box with the oxygen content measured using a Thermox Oxygen Analyzer (AMETEK Process & Analytical Instruments, Pittsburgh, PA 15238) on a Newport Optical Table (Newport Corporation, Irvine CA 92606). Laser

5   powers were measured using a Scientech D200 Power meter with PHF25 power meter heads (Scientech Inc. Boulder CO, 80303-1399). The contact photolithography at 157 nm exposure wavelength apparatus is shown in Figures 13, 14 and 15.

For contact photolithography at 157 nm exposure wavelength the

10   mask used were SPI Copper TEM Grids (SPI Inc. West Chester PA, 19380) , 3mm diameter x 50 mesh, were placed end to end across the entire wafer in the beam exposure path. The photoresist coated wafer was then exposed in sequential locations across the wafer to increasing exposure doses. After exposure the contact masks were removed from

15   the wafer.

Post Exposure Bake, Development and Characterization

The 157nm exposure was followed by a Post Exposure Bake, PEB, at 105 °C for 60 seconds. The samples were developed using Shipley LDD-26W Developer (Shipley Company, L.L.C., Marlborough MA 01752),

20   by being completely submerged in the developer for 60 seconds at room temperature. Then the sample was submerged in deionized (D.I.) water for 10 to 15 seconds, removed from the water bath, rinsed with D.I. water then blown dry with nitrogen gas. Then the samples were visually and microscopically evaluated for printing performance. The E0 clearing dose

25   was evaluated from regions in which there was not contact mask present, and the E1 Printing dose was evaluated from the regions directly below the contact mask.

Table 1. Absorbance/Centimeter (A/cm)

Ex. #	Fig #	Material	A/cm 157nm	A/cm 193nm	Thick. um	ppm O2	ppm H2O	As Rec'd	Load in	Shake H2O	Mol. Sieve	Bulb to Bulb
C1	2	Hexafluoro propylene Cyclic Dimer	980	-1.8	6/25			X	Air			
C1	2	Hexafluoro propylene Cyclic Dimer	>500	0.942	6/25/100			X	Air			
C2	3	Perfluoro-2-methylpentane	16	0.16	25/100/500			x	N₂			
C3	4	Perfluorooctane, CF3(CF2)6CF3	>>100	4	25/100/500u			x	N₂			
C4	5	Perfluorononane CF3(CF2)7CF3	>>100	30	25/100/500			x	N₂			
C5	6	Perfluoro(1,3-dimethyl cyclohexane)	329	1	25/100			x	Air			
C6	7	Perfluoro-trans-decalin	>1000	2	25/100			x	Air			
1A	8	Perfluoro-n-hexane, CF3(CF2)4CF3	9.13	0.41	500/920/2200		5.5 ppm	x	Air			
1B	8	Perfluoro-n-hexane, CF3(CF2)4CF3	1.48	0.42	500/920/2200		5.5 ppm	x	Air			
1C	8	Perfluoro-n-hexane, CF3(CF2)4CF3	3.71	0.32	500/920		9.1		N₂	X		

Ex. #	Fig #	Material	A/cm 157nm	A/cm 193nm	Thick. um	ppm O2	ppm H2O	As Rec'd	Load In	Shake H2O	Mol. Sieve	Bulb to Bulb
					/2200							
1D	8	Perfluoro-n-hexane, CF3(CF2)4CF3	1.14	0.008	500/92 0 /2200		<0.1		N_2	X	X	
1E	8	Perfluoro-n-hexane, CF3(CF2)4CF3	0.70	0.27	500/92 0 /2200				N2			X
2A	9	Perfluoro-n-pentane, CF3(CF2)3CF3	4.23	0.24	500/92 0 /2200			X	Air			
2B	9	Perfluoro-n-pentane, CF3(CF2)3CF3	0.97	0.21	500/92 0 /2200			X	N_2			
2C	9	Perfluoro-n-pentane, CF3(CF2)3CF3	0.81	0.24	100/50 0/ 920				N_2	X		
2D	9	Perfluoro-n-pentane, CF3(CF2)3CF3	0.50	0.04	100/50 0/ 920				N_2	X	X	
3B	10	Perfluoro-n-hexane, CF3(CF2)4CF3	0.17	0.03	500/22 00/600 0				N_2		X	
4B	11	Perfluoro-n-hexane, CF3(CF2)4CF3	1.33	0.23	100/50 0/ 1450				N_2		X	
C3	18	Perfluorooctane, CF3(CF2)6CF3	59.3	0.16	25/100/ 500				N_2		X	

Table 2. Index of Refraction and Temperature Coefficient of the Index at Lithographic Wavelengths.

Example	Figure	Immersion Fluid	Property	Temperature	157 nm	193 nm	248 nm
4C	12	Perfluoro-n-hexane, CF3(CF2)4CF3	Index of Refraction	31 °C	1.312	1.279	1.262
4C		Perfluoro-n-hexane, CF3(CF2)4CF3	Index of Refraction	21.5 °C	1.315,62 +/- 1×10^{-4}		
4C		Perfluoro-n-hexane, CF3(CF2)4CF3	dn/dT	21.5 °C	-5.83×10^{-4} /°C		

Table 3. Results of Contact Photolithography at 157 nm exposure wavelength With and Without The Use Of Immersion
5 Fluids

Example	Figure	Immersion Fluid	Fluid Path Length (mm)	E_o Dose (mJ/cm^2)	E_1 Dose (mJ/cm^2)
4	16	Perfluoro-n-hexane, CF3(CF2)4CF3	1	14	20
4	17	None	0	10	12

COMPARATIVE EXAMPLE 1

Hexafluoropropylene cyclic dimer was obtained from DuPont as Vertrel®
245.

The absorbance/centimeter of the sample was determined using the
5   relative transmission method with cell thicknesses of 6/25 micrometers, using
the methods discussed above. The sample was as received, which was
loaded in air. The optical absorbance per centimeter at 157 nm was 980/cm,
and the optical absorbance per centimeter at 193 nm was −1.9/cm. The
results are shown in Figure 2 and summarized in Table 1.

10   The absorbance/centimeter of the second sample was determined
using the relative transmission method with cell thicknesses of 6/25/100
micrometers, using the methods discussed above. The sample was as
received, which was loaded in air. The optical absorbance per centimeter at
157 nm was >500/cm, and the optical absorbance per centimeter at 193 nm
15   was 0.942/cm. The results are shown in Figure 2 and summarized in Table 1.

COMPARATIVE EXAMPLE 2

Perfluoro-2-methylpentane was purchased from SynQuest
Laboratories, Inc., Alachua, Florida (Perfluoro-2-methylpentane, 99% min.,
catalog #1100-2-10).

20   The absorbance/centimeter of the sample was determined using the
relative transmission method with cell thicknesses of 25/100/500 micrometers,
using the methods discussed above. The sample was as received, which was
loaded in a nitrogen environment. The optical absorbance per centimeter at
157 nm was 16/cm, and the optical absorbance per centimeter at 193 nm was
25   0.16/cm. The results are shown in Figure 3 and summarized in Table 1.

COMPARATIVE EXAMPLE 3

Perfluorooctane was purchased from SynQuest Laboratories, Inc.,
Alachua, Florida (Octadecafluoro-n-octane, 99% min., catalog #1100-2-14).

The absorbance/centimeter of the sample was determined using the
30   relative transmission method with cell thicknesses of 25/100/500 micrometers,
using the methods discussed above. The sample was as received, which was
loaded in a nitrogen environment. The optical absorbance per centimeter at

157 nm was >>100/cm, and the optical absorbance per centimeter at 193 nm was 4/cm. The results are shown in Figure 4 and summarized in Table 1.

Perfluorooctane was distilled through a grease-free stainless steel packed column until the purity of the perfluorooctane was brought up to

5 99.83% as measured by FID GC.

A small sample of 3A molecular sieves in a Hastelloy™ tube was heated to 300 to 350°C overnight under an N2 flow. The gas was stopped and then the Hastelloy™ tube sealed at both ends and allowed to cool to room temperature. The sealed Hastelloy™ tube was transferred to a nitrogen glove

10 bag. One end of the Hastelloy™ tube was unsealed and about 7 ml of dried sieves transferred to a vial (VWR TraceClean™ vial with a Teflon™ cap liner) containing ~15 ml of the 99.83% pure perfluorooctane prepared above.

The absorbance/centimeter of the 99.83% pure perfluorooctane treated with 3A molecular sieves was determined using the relative transmission

15 method with cell thicknesses of 25/100/500 micrometers, using the methods discussed above. The sample was exposed to 3A molecular sieves and was loaded in a nitrogen environment. The optical absorbance per centimeter at 157 nm was 59.3/cm, and the optical absorbance per centimeter at 193 nm was 0.16/cm. The results are shown in Figure 18 and summarized in Table 1.

20 This material is useful for immersion photolithography at 157 nm exposure wavelength at 193 nm.

For comparison purposes the absorbance/centimeter of the 99.83% pure perfluorooctane was also determined before its treatment with 3A molecular sieves. Relative transmissions were measured using cell

25 thicknesses of 100/500/1450 micrometers. The sample was loaded in a nitrogen environment. The optical absorbance per centimeter at 157 nm was 120.5, and the optical absorbance per centimeter at 193 nm was 20.0. The results are shown in Figure18. Since pure water has no significant absorbance at 193 nm, the decrease in 193 nm absorbance that occurs on

30 treatment with 3A molecular sieves reflects in this case the chemical absorption of impurities other than water.

COMPARATIVE EXAMPLE 4

Perfluorononane was purchased from SynQuest Laboratories, Inc., Alachua, Florida (Perfluorononane, 99% min., catalog 1100-2-18)

The absorbance/centimeter of the sample was determined using the
5   relative transmission method with cell thicknesses of 25/100/500 micrometers, using the methods discussed above. The sample was as received, which was loaded in a nitrogen environment. The optical absorbance per centimeter at 157 nm was >>100/cm, and the optical absorbance per centimeter at 193 nm was 4/cm. The results are shown in Figure 5 and summarized in Table 1.

10   COMPARATIVE EXAMPLE 5

Perfluoro(1,3-dimethylcyclohexane) was purchased from SynQuest Laboratories, Inc., Alachua, Florida (Perfluoro-1,3-dimethylcyclohexane, 98% min., catalog 1200-2-07).

The absorbance/centimeter of the sample was determined using the
15   relative transmission method with cell thicknesses of 25/100 micrometers, using the methods discussed above. The sample was as received, which was loaded in air. The optical absorbance per centimeter at 157nm was 329/cm, and the optical absorbance per centimeter at 193 nm was 1/cm. The results are shown in Figure 6 and summarized in Table 1.

20   COMPARATIVE EXAMPLE 6

Perfluoro-trans-decalin was purchased from Aldrich, Milwaukee, Wisconsin (trans-Perfluorodecalin, 98%, catalog #42,268-1).

The absorbance/centimeter of the sample was determined using the relative transmission method with cell thicknesses of 25/100 micrometers,
25   using the methods discussed above. The sample was as received, which was loaded in air. The optical absorbance per centimeter at 157 nm was >1000/cm, and the optical absorbance per centimeter at 193 nm was 2/cm. The results are shown in Figure 7 and summarized in Table 1.

EXAMPLE 1

30   Example 1A

The absorbance/centimeter of the perfluoro-n-hexane sample was determined using the relative transmission method with cell thicknesses of 500/920/2200 micrometers, using the methods discussed above. The sample

was as received, which was loaded in air. The optical absorbance per centimeter at 157 nm was 9.13/cm, and the optical absorbance per centimeter at 193 nm was 0.41/cm. The results are shown in Figure 8 and summarized in Table 1.

5   Example 1B

The absorbance/centimeter of the perfluoro-n-hexane of Example 1A was determined following the same procedures as in Example 1A with the exception that the samples were handled in a nitrogen rather than an air atmosphere. The optical absorbance per centimeter at 157 nm was 1.48/cm,

10   and the optical absorbance per centimeter at 193 nm was 0.42/cm. The results are shown in Figure 8 and summarized in Table 1.

Example 1C

The absorbance/centimeter of the perfluoro-n-hexane of Example 1A was determined using the method of Example 1B except that prior to

15   measurement, the perfluoro-n-hexane sample was shaken with water and was loaded in a nitrogen environment. The optical absorbance per centimeter at 157 nm was 3.71/cm, and the optical absorbance per centimeter at 193 nm was 0.32/cm. The results are shown in Figure 8 and summarized in Table 1.

Example 1D

20   The absorbance/centimeter of the perfluoro-n-hexane of Example 1A was determined using the method Example 1B except that the sample was shaken with water, exposed to 3A molecular sieves and was loaded in a nitrogen environment. The optical absorbance per centimeter at 157 nm was 1.14/cm, and the optical absorbance per centimeter at 193 nm was 0.008/cm.

25   The results are shown in Figure 8 and summarized in Table 1.

Example 1E

The perfluoro-n-hexane of Example 1A was purified by bulb to bulb distillation. Clean, grease-free glassware was used. Seals were made using grease-free Viton™ o-rings positioned so that liquid phase fluid never comes

30   in contact with the o-rings. A quartz tube 1" in diameter by 22" long was packed with an inch of stainless steel turnings. These turnings were located about 6" from the bottom end of the tube and were packed tight enough to provide support for a 6" high bed of 3A molecular sieves. A 100 ml flask,

equipped with a vacuum stopcock side arm adapter to N2/air/vacuum lines, was attached to the bottom end of the quartz tube.

The quartz tube was then placed in a furnace so that the 6" column of molecular sieves ended up entirely in a 12" long heater zone. A flow of air was started through the furnace and the molecular sieves were heated to 500°C for 2 hours. The air flow was changed for a nitrogen flow that had been passed through a liquid N2 trap and the furnace cooled to 100°C. The nitrogen flow was stopped, a 100 ml flask connected to the top end of the quartz tube via a detachable vacuum stopcock, and pump vacuum applied to the whole system while the flask and stopcock at the top of the quartz tube were heated with a forced air gun. The apparatus was then allowed to cool to room temperature under vacuum. The vacuum was relieved and 50 ml of perfluoro-n-hexane added to the flask at the bottom of the quartz tube. The system was resealed and the perfluoro-n-hexane frozen by application of a liquid nitrogen bath. Pump vacuum was pulled and system sealed off under vacuum. The perfluoro-n-hexane was then allowed to thaw so that dissolved oxygen could escape into the surrounding vacuum. The perfluoro-n-hexane was refrozen and high vacuum reapplied, removing evolved oxygen from the system. This freeze thaw cycle was repeated another two times.

After the end of the third such freeze-thaw cycle, the perfluoro-n-hexane was refrozen and a fresh vacuum pulled. The system was sealed off under vacuum and the liquid nitrogen cooling bath transferred from the flask containing the perfluoro-n-hexane to the empty flask at the top of the quartz tube. As the perfluoro-n-hexane warmed towards room temperature, it distilled under its own vapor pressure through the bed of 3A molecular sieves (absorbing water) and condensed relatively dry and oxygen free in the liquid nitrogen chilled flask at the top of the quartz tube.

Once distillation was complete, the receiving flask was allowed to warm to room temperature, the system back filled with pure nitrogen, the valve at the top of the receiving flask closed off, and the flask disconnected from the system. The flask was then transferred to a glove box with pure nitrogen atmosphere where the flask was opened and absorption measurements carried out.

39

The absorbance/centimeter of the sample was determined using the
following the method of Example 1B. The sample underwent bulb to bulb
distillation and was loaded in a nitrogen environment. The optical absorbance
per centimeter at 157 nm was 0.70/cm, and the optical absorbance per

5   centimeter at 193 nm was 0.27/cm. The results are shown in Figure 8 and
summarized in Table 1.

EXAMPLE 2

Example 2A

Perfluoro-n-pentane was purchased from SynQuest Labortories, Inc.,

10   Alachua, Florida (Dodecafluoro-n-pentane, 99% min., catalog 1100-2-05)
The absorbance/centimeter of the sample was determined using the
method Example 1A. The sample was as received and was loaded in air. The
optical absorbance per centimeter at 157 nm was 4.23/cm, and the optical
absorbance per centimeter at 193 nm was 0.24/cm. The results are shown in

15   Figure 9 and summarized in Table 1.

Example 2B

The absorbance/centimeter of the sample was determined using the
method of Example 1B The sample was as received and was loaded in a
nitrogen environment. The optical absorbance per centimeter at 157 nm was

20   0.97/cm, and the optical absorbance per centimeter at 193 nm was 0.21/cm.
The results are shown in Figure 9 and summarized in Table 1.

Example 2C

The absorbance/centimeter of the sample was determined using the
method of Example 1C. The sample was shaken with water, and was loaded

25   in a nitrogen environment. The optical absorbance per centimeter at 157 nm
was 0.81/cm, and the optical absorbance per centimeter at 193 nm was
0.24/cm. The results are shown in Figure 9 and summarized in Table 1.

Example 2D

The absorbance/centimeter of the sample was determined using the

30   method of Example 1D. The sample was shaken with water, exposed to 3A
molecular sieves and was loaded in a nitrogen environment. The optical
absorbance per centimeter at 157 nm was 0.50/cm, and the optical

absorbance per centimeter at 193 nm was 0.04/cm. The results are shown in Figure 9 and summarized in Table 1.

EXAMPLE 3

Example 3A: Preparation of Perfluoro-n-hexane Sample

5   A 10 gallon sample of perfluoro-n-hexane (DuPont Zonyl(TM) PFH) was distilled through a 45 foot tall stainless steel column packed with ¼" stainless steel ProPak(TM) under 3.8 psi (18.5 psia) of helium over the course of several days. Product was collected in stainless steel cylinders. Sixty-three cuts were taken.   Cuts #61 -63, bp 63.2C under 3.8 psi (18.5 psia) helium,

10   were combined giving a total sample weight of 10.7 lbs. GC/MS analysis using a 105 meter capillary column [0.32 mm i.d. coated with a 3 micron film of RTX-1 (Restek DB-1 column)] found 99.99922 % perfluoro-n-hexane and 0.00078% perfluoro-n-pentane (area percents from a flame ionization detector). Combined cuts #61- 63 were found to exhibit absorption of A/cm of

15   1.29 at 157 nm when measured under nitrogen. The combined cuts #61-63 were then redistilled using an all-new 6' tall, vacuum jacketed glass column packed with 1/8" ProPak. This distillation was done under a positive pressure of helium (~14.7 psia). No grease of any sort was used in the assembly of this apparatus. Teflon(TM) sleeves were used at the joints. Thirteen cuts were

20   taken, product being collected in VWR TraceClean(TM) bottles with 0.0125" Teflon(TM)/silicone cap liners. Fraction #13, bp = 57.6°C, weighed 229 grams, and analyzed 99.99957% perfluoro-n-hexane by GC/MS.

       A small sample of 3A molecular sieves in a Hastelloy™ tube was heated to 500°C for 2 hours under airflow. The air flow was stopped and then

25   the Hastelloy™ tube was sealed at both ends and allowed to cool to room temperature. The sealed Hastelloy™ tube was transferred to a nitrogen glove bag. One end of the Hastelloy™ tube was unsealed and about 7 ml of the dried 3A sieves transferred to a vial (VWR TraceClean™ vial with a Teflon™ cap liner) containing about 15 ml of the 99.99957% pure perfluoro-n-hexane

30   prepared above.

       Example 3B: Transparency Results for 99.99957% Pure Perfluoro-n-hexane.

The absorbance/centimeter of the sample was determined using the relative transmission method with cell thicknesses of 500/2200/6000 micrometers, using the methods discussed above. The sample exposed to 3A molecular sieves above was loaded in a nitrogen environment. The optical
5   absorbance per centimeter at 157 nm was 0.17/cm, and the optical absorbance per centimeter at 193 nm was 0.03/cm. The results are shown in Figure 10 and summarized in Table 1.

EXAMPLE 4

Perfluoro-n-hexane, CF3(CF2)4CF3

10   Perfluoro-n-hexane (DuPont Zonyl™ PFH) was distilled through a grease-free stainless steel packed column until the purity of the perfluoro-n-hexane was brought up to 99.69% as measured by FID GC.

        3A molecular sieves were activated by heating overnight at 500°C in air. These activated molecular sieves were added to about 4X their volume of
15   the 99.69% pure perfluoro-n-hexane.

Example 4B

        The absorbance/centimeter of the sample was determined using the relative transmission method with cell thicknesses of 100/500/1450 micrometers, using the methods discussed above. The sample exposed to 3A
20   molecular sieves was loaded in a nitrogen environment. The optical absorbance per centimeter at 157 nm was 1.33/cm, and the optical absorbance per centimeter at 193 nm was 0.23/cm. The results are shown in Figure 11 and summarized in Table 1.

Example 4C

25   The index of refraction and its temperature coefficient was determined by the methods described above. The index of refraction at 157 nm and 31 °C was 1.312 and at 21.5 °C was 1.31562, and dn/dT was -5.83×10^{-4}.

Example 4D: 157 nm Contact Immersion Photolithography at 157 nm exposure wavelength

30   157 nm contact immersion photolithography at 157 nm exposure wavelength was performed with the perfluoro-n-hexane immersion fluid at a depth (or optical path length in the fluid) of 1mm. An optical micrograph of the lithographically printed image in the photoresist on the semiconductor wafer is

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shown in Figure 16. The E0 clearing dose was 14 mJ/cm^2 and the E1 printing dose was 20 mJ/cm^2, the results are summarized in Table 3. The perfluoro-n-hexane was compatible with the photoresist, its latent image formation process, and did not interfere with the development and printing process.

Comparative Example 7: 157 nm Contact Photolithography at 157 nm exposure wavelength

For comparison, 157 nm Contact Photolithography at 157 nm exposure wavelength was also performed without the use of an immersion fluid. An optical micrograph of the lithographically printed image in the photoresist on the semiconductor wafer is shown in Figure 16. The E0 clearing dose was 10 mJ/cm^2 and the E1 printing dose was 12 mJ/cm^2. The high optical transparency of the immersion fluid lead to little change in the E0 and E1 doses for dry or wet contact photolithography at 157 nm exposure wavelength.

Example 5

Deoxygenation of Perfluoro-n-hexane

Progress in the deoxygenation of perfluoro-n-hexane was followed using an Ocean Optics Inc. optical fiber oxygen sensor (FOXY 18-G), which employs 470 nm light to stimulate 600 nm fluorescence in a ruthenium sensor in a process, which is quenched by oxygen. The high concentration calibration point was determined by performing a gas saturation experiment from which it was determined that the oxygen saturation concentration of perfluoro-n-hexane at one atmosphere and ca. 25°C was 104 ppm. The low oxygen concentration calibration point was determined in different ways depending upon the deoxygenation method being employed.

A. Sparging with Nitrogen

The low concentration limit of the FOXY probe was calibrated by placing the sensor into an atmosphere prepared from boiled off liquid nitrogen, which should contain essentially no oxygen. This was chosen as the zero point on the sensor.

Perfluoro-n-hexane equilibrated with air was placed in a glass vessel equipped with the FOXY oxygen probe, an inlet for nitrogen gas, and an outlet for nitrogen gas. A nitrogen flow was started through the perfluoro-n-hexane and the level of oxygen followed using the FOXY probe. The nitrogen flow

was deliberately slow, a small bubble roughly every second, so as to observe the effect. Dissolved oxygen concentration steadily dropped from 104 ppm to 0 ppm over about 19 minutes, that is, at the end point, the oxygen level of the perfluoro-n-hexane dropped from the saturation level to being

5   indistinguishable from that of the nitrogen stream.

B. Freeze Thaw Cycles

To calibrate the zero-point of the sensor, the FOXY probe was subject to a vacuum at 0.192 Torr.

10   A 50 ml flask loaded with 25 ml of perfluoro-n-hexane was attached to a vacuum line with a diffusion pump. The FOXY probe was introduced into the flask via a side arm sealed with an Ultra-Torr reducing union. The perfluoro-n-hexane was first degassed using freeze/thaw cycles (repeated cycles of freezing the perfluoro-n-hexane with liquid N2, pulling pump vacuum while the

15   perfluoro-n-hexane remained frozen, sealing off the flask, and then thawing). A series of calibration points was then determined according to the following method.

The perfluoro-n-hexane was then exposed to a low pressure of pure oxygen. At this point the FOXY probe, now set to read in torr of oxygen, found

20   154 ppm of oxygen in the gas phase above the perfluoro-n-hexane and 150 ppm oxygen when the ruthenium sol-gel tip of the probe was lowered and immersed in the liquid perfluoro-n-hexane. The probe was once again raised into the vapor phase after which the perfluoro-n-hexane was degassed by repeated freeze/thaw cycles. After the first cycle the vapor phase above the

25   perfluoro-n-hexane measured 15 torr of oxygen and then 6.5 torr, 4 torr, and 3.5 torr upon subsequent degassing cycles. Twelve hours after the last degassing cycle, the FOXY probe still read 3.5 torr oxygen in the vapor phase above the perfluoro-n-hexane. Using Henry's law [$X_{O2} = P_{O2}(torr)/144800$ where X is the mole fraction of oxygen dissolved in the perfluoro-n-hexane],

30   3.5 torr of oxygen in the vapor phase above the liquid perfluoro-n-hexane translates into about 2 ppm by weight O2 dissolved in the liquid perfluoro-n-hexane.

CLAIMS

What is claimed is:

1. A composition consisting essentially of a perfluoro-n-alkane characterized by a water concentration of less than 10 ppm, an oxygen concentration of less than 10 ppm, and an absorbance at 157 nanometers in the range of 0.1 to 10 cm^{-1}, said perfluoro-n-alkane selected from perfluoro-n-pentane, perfluoro-n-hexane, and mixtures thereof.

2. The composition of Claim 1 wherein said perfluoro-n-alkane is characterized by an oxygen concentration of less than 5 ppm, a water concentration of less than 5 ppm, and an absorbance at 157 nm in the range of 0.1 to 2 cm^{-1}.

3. The composition of Claim 2 wherein said perfluoro-n-alkane is characterized by an oxygen concentration of less than 1 ppm, a water concentration of less than 5 ppm, and an absorbance at 157 nm of 0.1 to 1 cm^{-1}.

4. A process for preparing a perfluoro-n-alkane liquid characterized by a water concentration of less than 10 ppm, an oxygen concentration of less than 10 ppm, and an absorbance at 157 nanometers in the range of 0.1-10 cm^{-1}, the process comprising subjecting a perfluoro-n-alkane liquid to at least one extraction step, wherein said perflurooalkane liquid is selected from perfluoro-n-pentane, perfluoro-n-hexane, and mixtures thereof.

5. The process of Claim 4 wherein said process is carried out in an oxygen-minimized atmosphere.

6. The process of Claim 4 or 5 comprising fractional distillation of a perfluoro-n-alkane liquid of at least 99% purity, contacting a heart cut condensate obtained therefrom with an absorbent, said absorbent being selected from silica gel, zeolite molecular sieves, and mixtures thereof.

7. The process of claim 6 further comprising purifying and activating said absorbent prior to contacting said condensate therewith by heating said absorbent in an oxidizing atmosphere to a temperature sufficient to remove substantially all water from said absorbent, then cooling and sealing the absorbent in an oxygen-minimized atmosphere.

8.   The process of Claim 6 wherein said absorbent is a mixture of absorbents.

9.   The process of claim 6 wherein said absorbent comprises one or more zeolite molecular sieves.

10.   The process of Claim 9 wherein said zeolite molecular sieves are selected from 3A, 4A, and 5A zeolite molecular sieves.

11.   The process of Claim 6 wherein said distillation is conducted in a grease-free distillation system.

12.   The process of Claim 6 wherein said absorbent is a mixture of absorbents, wherein said distillation is conducted in a grease-free distillation system, and further comprising the step of purifying and activating said absorbents prior to contacting said condensate therewith by heating said absorbents in an oxidizing atmosphere to about 500 °C, followed by cooling and sealing in an inert, oxygen-minimized atmosphere.

13.   A perfluoro-n-alkane prepared by the process of claim 4.

FIG. 1

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FIG. 12

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FIG. 13

FIG. 14

FIG. 15A

FIG. 15B

FIG. 16

FIG. 17

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